

5. X-Ray Diffuse Scattering

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In this research program, modern x-ray scattering techniques are used to study the structures and phase transitions in novel states of condensed matter. We have two principal experimental facilities. At M.I.T. we have three high-resolution computer controlled x-ray spectrometers using either a conventional or high intensity rotating anode x-ray generator. The angular resolution can be made as fine as 1.8 seconds of arc; this enables one to probe the development of order from distances of the order of the x-ray wavelength, $\sim 1 \text{ \AA}$, up to $30,000 \text{ \AA}$. The sample temperature may be varied between 2 K and 500 K with a relative accuracy of $2 \times 10^{-3} \text{ K}$. We are currently installing a two spectrometer system at the National Synchrotron Light Source at Brookhaven National Laboratory. This makes possible high resolution scattering experiments with a flux more than three orders of magnitude larger than that from a rotating anode x-ray generator. This opens up a new generation of experiments. Synchrotron x-ray scattering experiments are also carried out on a wiggler beam line at the Stanford Synchrotron Radiation Laboratory.

As part of the JSEP program we have built an x-ray compatible high vacuum single crystal apparatus. This enables us to use synchrotron radiation to study the structure and transitions occurring at single surfaces; such experiments are now being initiated. Our current experiments in this program are concentrated in three areas: (i) the growth, structure, and phase transitions of intercalant materials, most especially bromine-intercalated graphite, (ii) the structure and phase transitions of smectic liquid crystals, (iii) the evolution from thin film to bulk structures of model systems.

5.1 Intercalation Compound Structures and Transitions

Intercalation compounds represent a family of materials in which a foreign species (e.g., Br_2) is inserted between the layers of a lamellar material such as graphite. If the intercalant enters every n th layer then the resultant material is referred to as a stage- n intercalation compound. In this program we study both the intercalation process itself and the structure and transitions of the intercalation compound as a function of temperature, concentration, and stage index. Our work to date has

concentrated on the systems bromine-intercalated graphite $C_{7n}Br_2^{1-3}$ and potassium-mercury intercalated graphite.

The intercalate plane is found to have three sublattices and each sublattice has a centered ($\sqrt{3} \times 7$) rectangular structure with four Br_2 molecules per 2D unit cell in the commensurate phase. The coherently ordered in-plane bromine regions exceed 10,000 Å in size. In the stage-4 material a commensurate-incommensurate (CIT) transition is observed at $342.20 \pm 0.05^\circ K$. In the incommensurate phase, a stripe domain pattern becomes established in a single domain of a sublattice along the 7-fold direction. The incommensurability as a function of reduced temperature exhibits power law behavior with an exponent of 0.50 ± 0.02 confirming existing theories. The relative shifts observed for the various harmonics are accurately predicted by a sharp domain wall with $4\pi/7$ phase shifts. The intercalate layer exhibits a continuous melting transition from a two-dimensional solid phase to a smectic liquid crystal phase, occurring at $373.41 \pm 0.10^\circ K$ for a stage-4 compound. In the incommensurate phase it is predicted that the superlattice peaks should be power law singularities of the form $(Q - Q_n)^{-2 + x_n}$ where $x_n = \frac{2n^2}{49}$ and n is the order of the harmonic. To probe these line-shape effects we have carried out a high resolution synchrotron study of a sample of $C_{28}Br_2$ grown "*in situ*". Dramatic changes are indeed seen in the intensities and shapes of the successive harmonic peaks. Quantitative analysis is currently underway to compare the data critically with the theory.

We have synthesized and studied stage 1 $KH_g - GIC$.² From *in situ* x-ray studies we have learned that the compound forms by successive intercalation of K and then, after several hours, further intercalation of K and H_g to yield the final $KH_g - GIC$ compound. We find a 2×2 RO hexagonal network for the KH_g .

5.2 Smectic Liquid Crystals

Liquid crystals are made up of rod-like molecules. In the nematic phase the axes of the molecules align parallel to each other but the center of mass of the molecules are still randomly distributed so that one has a pure fluid structure factor. In the smectic A and C phases a one-dimensional sinusoidal density wave is set up either along (A) or at an angle (C) to the molecular axis. Thus, these smectics are like solids in one direction and fluids in the other two. These systems exhibit particularly interesting phase transitions which present an important challenge to modern theories of critical phenomena. At lower temperatures many liquid crystal materials exhibit more ordered phases such as smectic B, F, and G. These have well-developed in-plane triangular order. If the order is truly long range then the phase is a plastic crystal. Otherwise, the smectic may be a realization of a novel phase of matter labelled a "stacked hexatic" with long range order in the crystalline axes but only short range order in the positions of the molecules. We have recently studied in some detail the smectic phases and phase transitions in a number of materials.⁴⁻⁶ Special emphasis has been given to multicritical behavior associated with the nematic-smectic A transition.

The nematic–smectic A transition was once thought to be always first order. However, a series of high resolution experiments, including our own, have shown that the opposite is the case and indeed the transition is usually continuous. However, thermodynamic data have suggested that if the temperature range over which the nematic phase is stable is sufficiently small then the nematic–smectic A transition is first order.

By studying the N–A transition in appropriate mixtures it is possible to monitor continuously this crossover from second to first order behavior. The crossover is believed to occur at a special point known as a "tricritical point". At the tricritical point, mean field theory should properly describe the critical behavior. We find that for concentrations near the tricritical point in the series alkoxy cyanobiphenyl (NCB) and pentylbenzenethioalkoxybenzoate ($\tilde{n}55$) new critical behavior is indeed observed with exponents which are at least close to the mean field values; there are some subtle, but real, discrepancies which require an extension of the theory.

We have carried out an extensive high resolution x-ray scattering study of the nematic–smectic $A(N-S_A)$ and reentrant nematic–smectic $A(RN-S_A)$ phase transition behavior in mixtures of octyloxycyanobiphenyl (80CB) and hexyloxycyanobiphenyl (60CB). The smectic A phase boundary is found to be parabolic in the temperature–concentration plane with a median temperature $T_M = 38.06^\circ\text{C}$ and a critical concentration $y_o = 0.427$; here y is the 60CB:80CB molecular ratio. Detailed studies of the smectic fluctuations in the nematic phase are reported for $y = 0.33, 0.413, 0.420, 0.429, 0.440$ and 0.443 . The first three concentrations exhibit $N-S_A$ and $RN-S_A$ transitions whereas in the latter three samples with decreasing temperature the smectic correlation lengths and susceptibility exhibit maxima at T_M and then decrease with a further decrease in temperature.

The data are analysed using an extension of the Pershan–Prost optimal density theory. All of the data are well-described by the phenomenological theory; the critical exponents so-obtained are $\nu_{\parallel} = 0.76 \pm 0.03$, $\nu_{\perp} = 0.62 \pm 0.05$ and $\gamma = 1.49 \pm 0.07$. These agree quantitatively with values obtained in single layer materials with comparable nematic ranges; thus the $N-S_A$ and $RN-S_A$ transitions are identical in character to conventional $N-S_A$ transitions provided that one includes the crossover effects inherent in the parabolic phase boundary. Studies of the in-plane fluid structure factor in the N , S_A and RN phases show that the mean molecular spacings and positional correlations are closely similar to those in single layer materials; in each phase the structure factor is well described by a circularly-averaged Lorentzian with a correlation length of 6.9 \AA . These results argue strongly against pairing models for the reentrant behavior. Our current preference is for models based on competing order parameters which are required to describe the varied behavior observed in other polar materials.

5.3 Structures and Transitions of Ultra-Thin Rare Gas Crystals

For a number of years we have been studying the structure and transitions of rare gas monolayers on graphite.^{7,8} This has yielded new information on the nature of melting in two dimensions and on two dimensional commensurate-incommensurate transitions. We have now begun studying the wetting characteristics of simple atoms and molecules on surfaces. Initial experiments on C_2H_4 on graphite show distinct layering transitions up to three layers and then a continuous evolution of the thickness to macroscopic values; the latter occurs in the liquid phase near the triple point. Initial studies of krypton on graphite indicate that in the solid phase the system grows layer by layer with the stacking of the layers in an fcc sequence even after three layers. Further, high resolution studies of this layer-by-layer growth are underway.

References

1. A. Erbil, A.R. Kortan, R.J. Birgeneau, and M.S. Dresselhaus, in M.S. Dresselhaus, G. Dresselhaus, J.E. Fisher, and M.J. Moran, (Eds.) *Intercalated Graphite*, Materials Research Society Symposia Proceedings, Vol. 20, (North-Holland Elsevier, New York 1982) p. 21.
2. A. Erbil, G. Timp, A.R. Kortan, R.J. Birgeneau, and M.S. Dresselhaus, *Synthetic Metals* 7, 273 (1983).
3. A. Erbil, A.R. Kortan, R.J. Birgeneau, and M.S. Dresselhaus, *Phys. Rev. B* 28, 6329 (1983).
4. B.M. Ocko, R.J. Birgeneau, J.D. Litster, and M.E. Neubert, *Phys. Rev. Lett.* 52, 208 (1984).
5. B.M. Ocko, A.R. Kortan, R.J. Birgeneau, and J.W. Goodby, *J. Physique* 45, 113 (1984).
6. A.R. Kortan, H. von Känel, R.J. Birgeneau, and J.D. Litster, *J. Physique* 45 (1984).
7. P.A. Heiney, P.W. Stephens, R.J. Birgeneau, P.M. Horn, and D.E. Moncton, *Phys. Rev. B* 28, 6416 (1983).
8. P.W. Stephens, P.A. Heiney, R.J. Birgeneau, P.M. Horn, D.E. Moncton, and G.S. Brown, *Phys. Rev. B*, 29, 3512 (1984).